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Structure–Reactivity Study of Mechanically Activated Zinc Ferrite

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Changes in the structure and reactivity of zinc ferrite as a result of mechanical activation and thermal relaxation have been studied. The transition of zinc ferrite into a metastable state is the result of the mechanically induced inversion and the partial deformation of the anion sublattice. The inversion is reversible and the stresses around the deformed bonds may relax during heating. Chemical changes serve as one possible channel of the relaxation. The deformation in octahedral geometry has been hypothetically connected to promotion of the Zn dissolution in diluted acids. A conception on the reason of high-temperature reactivity of mechanically activated zinc ferrite was suggested. © 1996 Academic Press, Inc.

1. INTRODUCTION

Over the past 20 years there has been a fairly extensive amount of work directed toward determining the way in which mechanically induced disordering influences the physical properties and chemical reactivity of solid substances (1–4). Due to the versatility of ferrites combined with the physical flexibility of their structure providing a wide range of physical behavior and chemical reactivity, they have been considered as very convenient model systems for the above investigation.

Detailed study of mechanically activated ferrites with close packed structural units has shown that, depending on the composition of the close packed sublattice and on the dimension of cations, energy-intensive grinding leads to various forms of structural failure (5–10). If large cations are present in the system, the translation invariance completely disappears and amorphization takes place. A characteristic feature of spinels containing relatively small cations is the possibility of preserving the long-range order. The transition of the above substances into a metastable state at grinding is assumed to be a result of a mechanically induced inversion during which some of the Fe^{3+} cations occupy free tetra-sites forbidden at equilibrium conditions and the Me^{2+} cations pass into octa-vacancies. The changes in the cation sublattice are accompanied by a lattice contraction resulting mainly in the alteration of the octa/cation–anion–octa/cation bond angles (11). The changes in the intersublattice exchange interactions are manifested in the magnetic properties of mechanically activated ferrites. As an example the change of paramagnetic zinc ferrite into a magnetically ordered state can be mentioned (5, 8, 11).

While the changes in magnetic properties of ferrites brought about by the above mentioned structural phenomena are discussed extensively in the literature, the chemical consequences are treated only in a limited extent (12–15). According to (9, 12, 13), the formation of a structurally metastable state in zinc ferrite brings about an energy accumulation from 40 to 65 $kJmol^{-1}$. At dissolution of mechanically activated ferrite in acids the ratio between the ions of zinc and iron transferred into solution is changed in comparison to the dissolution of nonactivated ferrite. This phenomenon is often taken as a measure for the determination of the threshold amount of specific grinding energy above which the transformation of ferrite into a metastable state occurs. Due to the importance ascribed to this phenomenon further research in this field is needed.

Another problem, which was studied only in a limited extent until now, is the problem of the thermal stability of mechanically induced structural defects and the mechanism of their relaxation on heating (16). The solving of this problem is of key importance for the explanation of high-temperature reactivity of mechanically activated ferrites and can find practical application in the use of mechanically activated zinc ferrite as an absorbent in high-temperature coal gas desulfurization process (17).

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In an attempt to contribute to the solution of the problems mentioned above, the present work is devoted to the structure–reactivity study of mechanically activated zinc ferrite and to the investigation of chemical changes taking place during the evolution of the mechanically disturbed structure on heating.

2. EXPERIMENTAL

2.1. Material

Zinc ferrite (Franklinite, JCPDS 22-1012) was prepared in the polycrystalline form by a solid state reaction. Stoichiometric mixtures of powdered reactants containing 66.34% α-Fe$_2$O$_3$ and 33.76% ZnO by weight (products of Merck) were homogenized in a ball mill. Loose powdered mixtures weighing 10 g were pressed into tablets 20 mm in diameter and 4 mm thick under a pressure of 30 MPa. The tablets were heated isothermally: heating was carried out in a preheated electric furnace, which was maintained at the temperature 1220 ± 5 K for 4.5 h. At the completion of the heat treatment period the samples were removed from the furnace and cooled rapidly by air quenching. The single phase nature of the as-prepared sample was confirmed by XRD analysis.

2.2. Methods

Zinc ferrite was activated by grinding in a planetary mill EI 2 × 150 (Institute of Solid State Chemistry, Novosibirsk). Two grams of the as-prepared sample were ground for 5, 12, and 24 min in a ceramic-covered grinding chamber. The volume of the grinding chamber was 150 ml. Balls made of α-Al$_2$O$_3$ ceramics with a diameter of 3 to 5 mm were used. The ball to powder weight ratio was 50:1. Grinding experiments were performed in air at 750 rpm.

The particle size distribution was measured by laser radiation scattering using the granulometer Laser-Particle-Sizer Analysette 22 (Fritsch, Idar-Oberstein). The mean particle diameter d_m was calculated as the first moment of the volume size distribution function. The specific surface area S was determined by the standard Brunauer–Emmett–Teller (BET) method using the apparatus Gemini 2360 (Sy-Lab, Vienna).

Scanning electron micrographs of the investigated samples were taken on a scanning electron microscope (SEM) BS-300 (Tesla, Brno) equipped with an energy dispersive X-ray spectrometer EDR 184 using the following operational parameters: acceleration voltage 25 kV, measuring time 120 s, working distance 45 mm, count rate 2000 cps.

X-ray diffraction measurements were carried out using an automatic SIEMENS-D500 diffractometer equipped with a graphite-crystal monochromator (in the diffracted beam) and controlled by an AUTOCOMPT computer using DIFRAC-AT software (developed by SOCABIM) and an ICDD-JCPDS database. A stabilized voltage of 35 kV and a current of 26 mA were used. Vertical divergence of X-ray beam (Co$K\alpha$ radiation) was restricted using two Soller's diaphragms. Horizontal divergence was 1°. Measurements were carried out in a vacuum of 0.2 Pa. Samples were measured on a platinum support which was heated to temperatures of 293–1000 K. The temperature was calibrated with melting standards to within ±5 K at the highest temperature. Temperature was checked by measuring and comparing the precisely known thermal expansion coefficient of Pt (18). After heating the sample to the selected temperature (the temperature jump experiment), the individual diffraction lines were taken in relatively short time intervals (8 min). Repeated measurements of the intensities of individual diffraction lines were stopped when the difference between the intensities measured in two consecutive steps was not apparent. This procedure took approximately 45 min at each temperature. Then the diffraction pattern itself was taken at the given temperature and this took 4 h at each temperature.

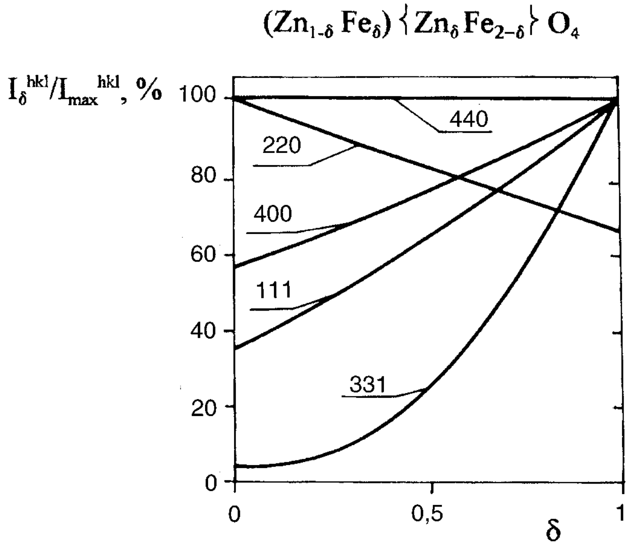

FIG. 1. Dependences of relative diffraction line intensities on the spinel inversion degree, δ, calculated for zinc ferrite (after Rykov *et al.* (9), reproduced with permission from authors).

The distribution of cations in the tetrahedral and octahedral sites of mechanically activated zinc ferrite was determined by an X-ray diffraction technique (9), in which the calculated value of intensity ratio between a pair of diffraction lines was compared with that observed (19, 20). The intensity ratios $I(220)/I(440)$ and $I(400)/I(440)$ have been used. The calculated dependence of relative diffraction line intensities on the spinel inversion degree of zinc ferrite is shown in Fig. 1.

The dissolution experiments were performed in a 500 ml glass reactor. Zinc ferrite samples of 226 mg were dissolved

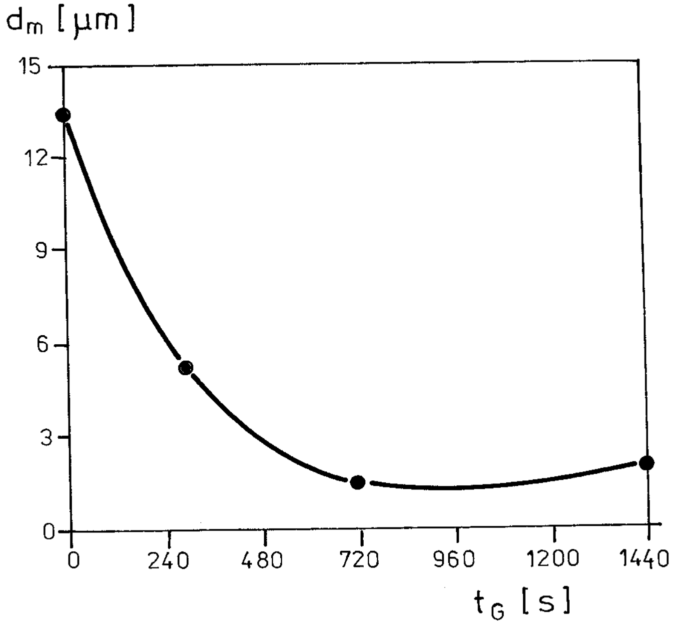

FIG. 2. Mean particle diameter, d_m, vs grinding time t_G.

in 200 ml of aqueous solution of sulfuric acid. The reaction mixture was held at a temperature of 363 K in accordance with data published in (15). The influence of the stirring rate on the initial rate of dissolution was investigated for dissolution of the as-prepared sample in 1.5 and 0.5 *N* sulfuric acid. Based on the obtained results the influence of mechanical activation on the dissolution kinetics was investigated at the stirring rate of $n = 14.83\ \mathrm{s}^{-1}$. Samples (1 ml) of the solution were withdrawn from the reactor at appropriate time intervals for determination of the percentage of dissolved metals by atomic absorption spectroscopy. The experimental results were fitted to the kinetic equation

$$kt_L = -\ln(1 - \alpha), \qquad [1]$$

where k is the rate constant. Equation [1] was assumed to be valid for ferrite dissolution with rate constant $k_{\mathrm{Zn+Fe}}$, as well as for the separate dissolution kinetics of zinc with k_{Zn} and iron with k_{Fe}, α is the dissolution degree and t_L is the reaction time.

3. RESULTS AND DISCUSSION

Figure 2 shows the changes in the mean particle diameter for the investigated time interval of grinding. The shape of the curve reflects not only fragmentation but also aggregation of fine particles at the later stages of grinding. Aggregation was also observed by SEM (compare Figs. 3a and 3b). While the as-prepared sample consists predominantly of individual particles, the sample ground for 24 min consists of aggregates. Stable aggregates behave under conditions of particle size analysis as individual particles and thus the "real" mean particle diameter is smaller than the determined value, $d_m = 1.97\ \mu\mathrm{m}$.

The grinding of zinc ferrite in a high-energy planetary mill is accompanied by changes of the shape of diffraction lines from the very beginning. The well-known phenomenon of diffraction line broadening and redistribution of diffraction line intensities is documented in Fig. 4. The inversion degree δ defined as the fraction of tetrahedral sites occupied by Fe^{3+} cations monotonically increases from the zero value of the as-prepared sample to 0.94 (see the sequence of open circles in Fig. 5). In other words, the normal spinel is, after 24 min of grinding, almost completely converted into an inverse one. A value $\delta = 0.67$ was found after 5 min of grinding by the method used in the present work and independently by the Rietveld structure refinement in our previous works (10, 11).

Complex of mechanically induced structural changes in zinc ferrite caused its gradual transition into a metastable state. The return into a low energy state is usually a thermally activated process.

The interval of thermal stability of mechanically induced defects in the structure of zinc ferrite was determined by the high-temperature XRD analysis in our previous work (16). We found that over the range from 293 to 600 K the shape of the diffraction patterns of activated samples remains the same. At temperatures over 600 K a gradual narrowing of diffraction lines as well as redistribution of their integral intensities takes place (Fig. 6). The thermally induced decrease in the inversion degree proceeding in the narrow temperature interval 760–820 K is demonstrated on the example of the 24 min ground sample by the sequence of the crosses in Fig. 5.

High-temperature XRD analysis revealed that the only process taking place in samples ground for 5 and 12 min is gradual recrystallization terminating at 1000 K by a total recovery of the structure. The processes taking place during heating of the sample activated for 24 min are more complex. It is evident from the comparison of the diffraction patterns of activated and as-prepared samples taken at 780 K (Figs. 7a and 7b) that the process of structural relaxation of the mechanically activated sample is accompanied by the partial decomposition of the ferrite into ZnO and $\mathrm{Fe_2O_3}$. Taking into account that zinc ferrite is synthesized from the above oxides at a 50% higher temperature, the extraordinarily high degree of the metastability of this sample is clearly demonstrated.

It follows from the above results that under the above conditions of grinding and heating the mechanically induced disordering of zinc ferrite has varied in a wide inter-

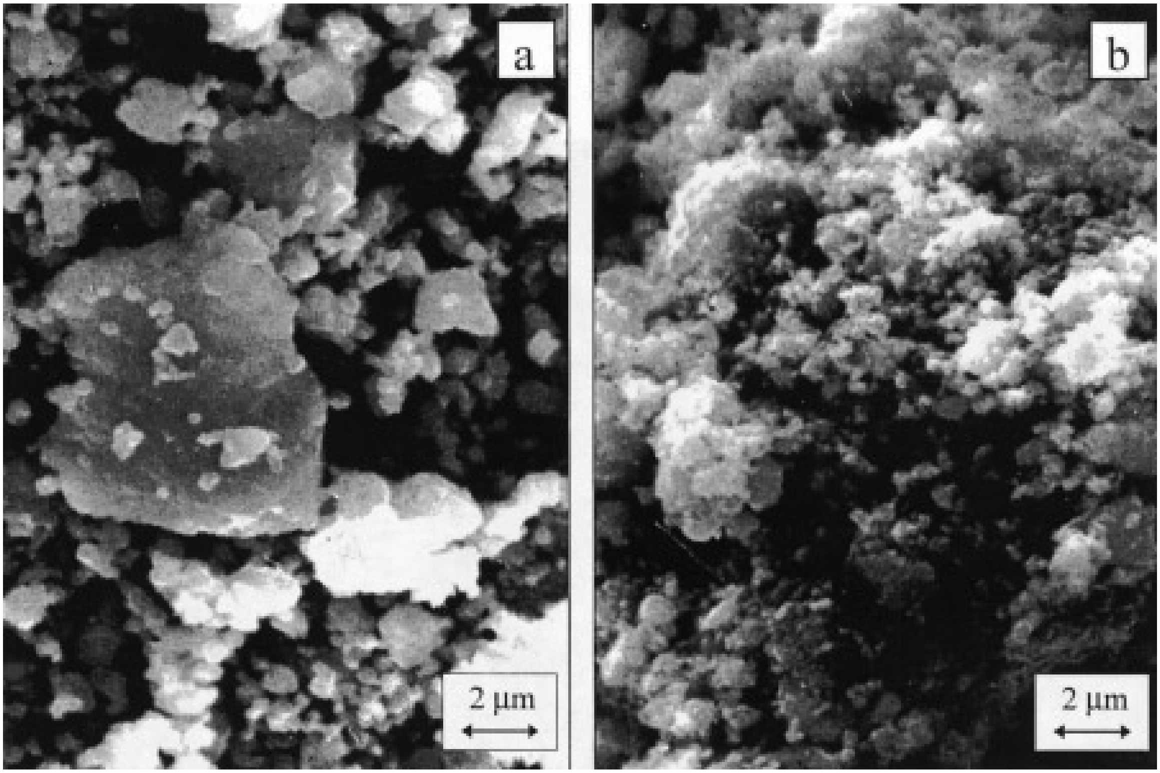

FIG. 3. Scanning electron micrograph of the as-prepared sample (a) and of the sample mechanically activated for 24 min (b).

val. A set of samples suitable for a structure–reactivity relationship study was prepared in this way.

According to (9, 12, 13) the mechanically induced transfer of cations into metastable positions can be identified by determining a change in the Zn/Fe ratio passing into the leachate during dissolution in acids. The results pre-

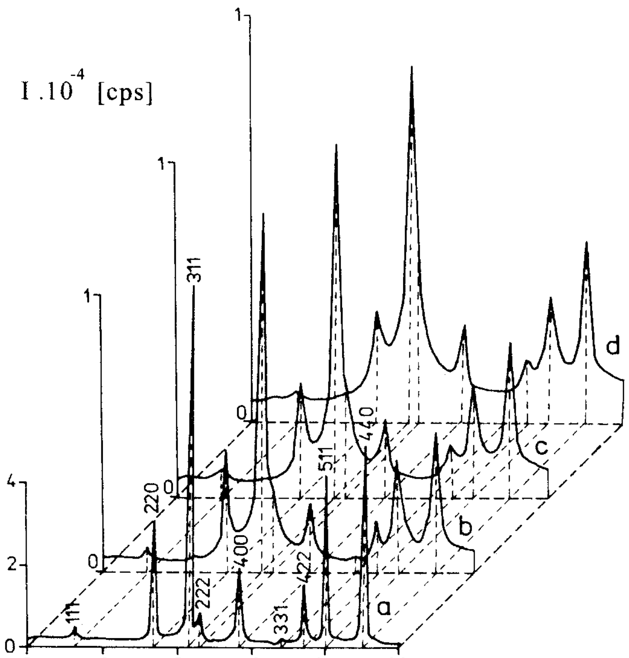

FIG. 4. X-ray diffraction patterns of the as-prepared sample (a) and of samples mechanically activated for 5 min (b), 12 min (c), and 24 min (d) (Mo$K\alpha$ radiation).

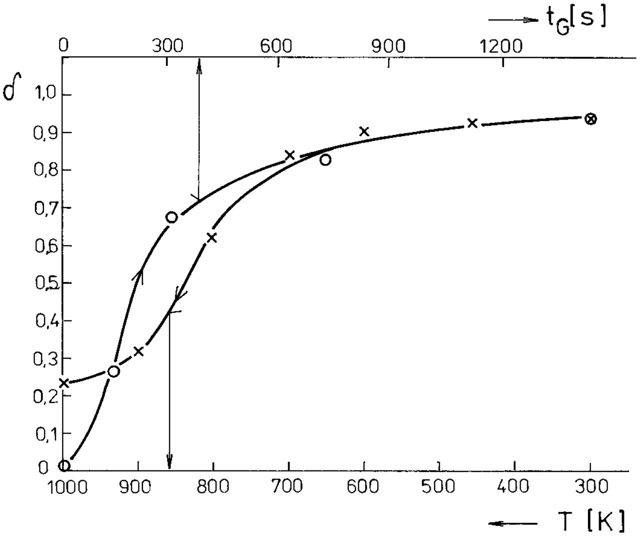

FIG. 5. Inversion degree, δ, vs grinding time t_G (open circles) and temperature T (crosses).

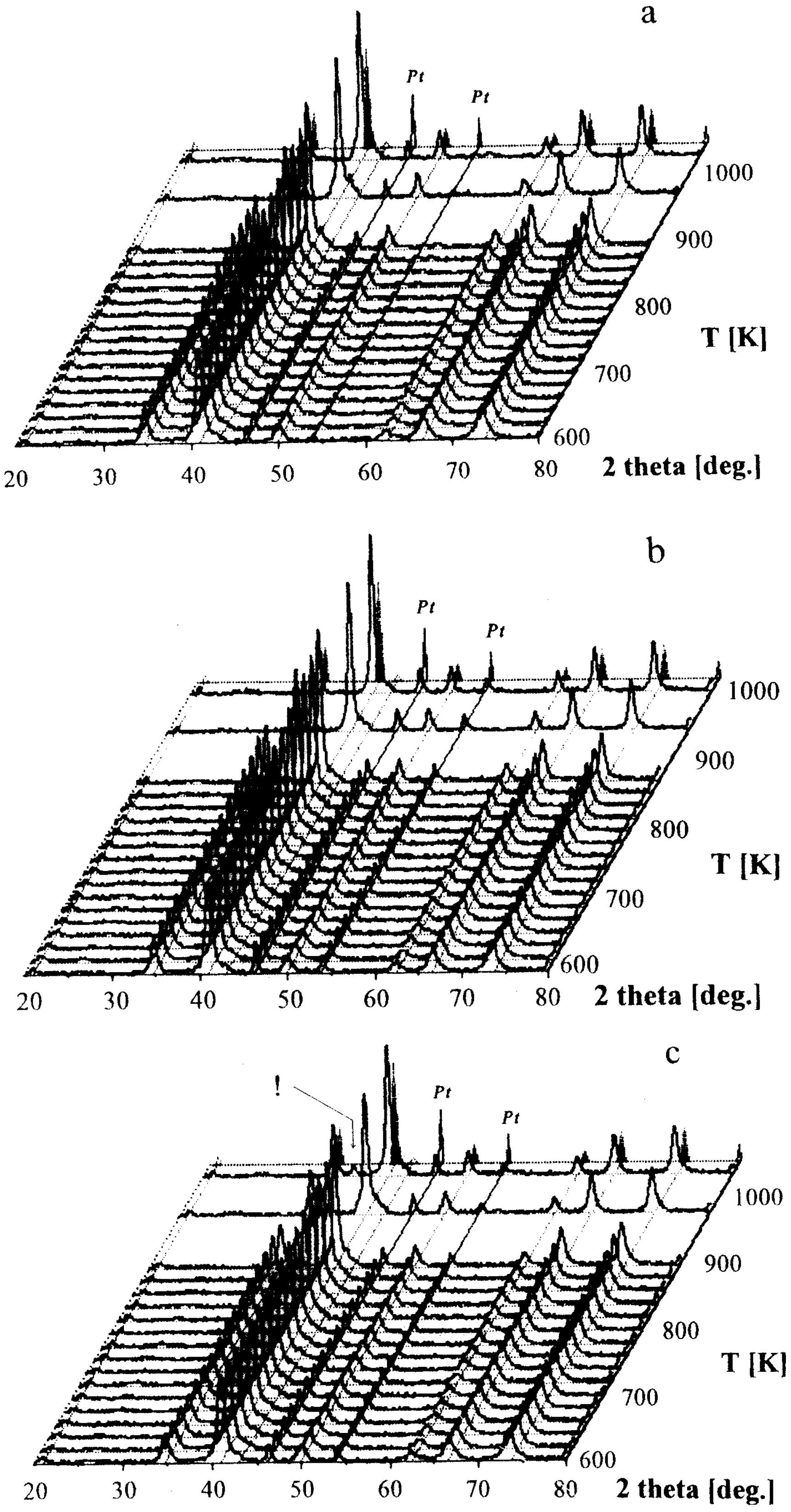

FIG. 6. Axonometric projection of the X-ray diffraction patterns of the thermal relaxation of zinc ferrite mechanically activated for 5 min (a), 12 min (b), and 24 min (c) (samples were measured on a platinum support, Co$K\alpha$ radiation).

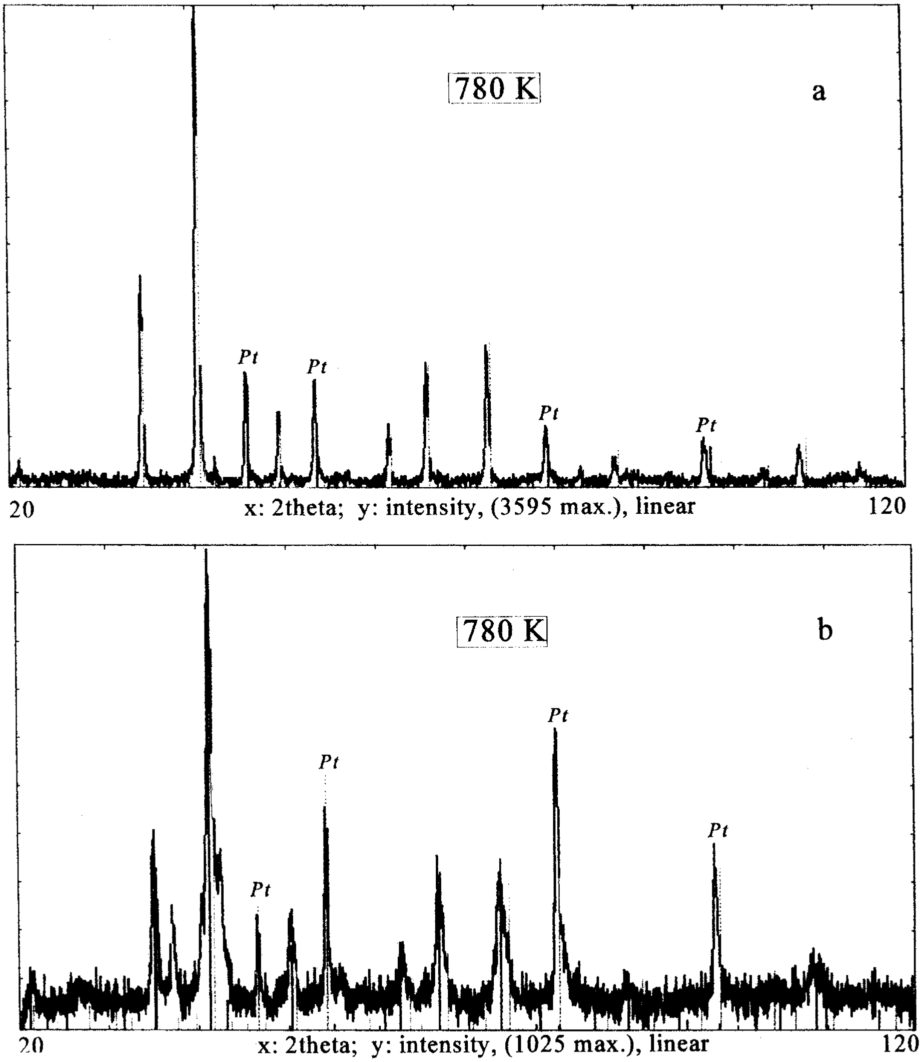

FIG. 7. Comparison of X-ray diffraction patterns for the as-prepared sample (a) and for the sample mechanically activated for 24 min (b) taken at 780 K (Co$K\alpha$ radiation).

sented in the above mentioned papers have shown that, during the dissolution of nonactivated ferrite, zinc is first to go into solution and followed by iron, whereas during the dissolution of mechanically activated ferrite, iron is dissolved before zinc.

The dissolution of the as-prepared sample revealed that the Zn/Fe ratio depends on the leaching time as well as on the concentration of the acid (Fig. 8). The Zn/Fe > 1 ratio corresponding to the above cited data for nonactivated zinc ferrite was determined in the initial stages of dissolution in a 1.5 *N* sulfuric acid. Dissolution in such a concentrated acid, however, is not convenient when investigating the differences in the selectivity of dissolution between the samples differing in the mechanically induced structural disordering. Taking into account the disadvantages of leaching in concentrated acid, the rate and selectivity of dissolution in 0.5 *N* H_2SO_4 was investigated. At dissolution of the as-prepared sample in the diluted acid the Zn to Fe ratio in the solute is constant in a wide time interval t_L and is equal to the stoichiometric one. The kinetics of the dissolution of Zn and Fe is illustrated on the example of the 24 min activated and subsequently heated samples in Fig. 9.

The chemical dissolution is a surface sensitive process. However, the influence of mechanically induced defects, their type, and their concentration on the dissolution kinetics was confirmed by numerous experiments. In simple oxides, sulfides, and carbonates, the promotion of dissolution and an increase in the dissolution heat due to amorphization has been shown (3, 21–23).

Assuming the specific features of the mechanically induced disordering in zinc ferrite, the influence of the spe-

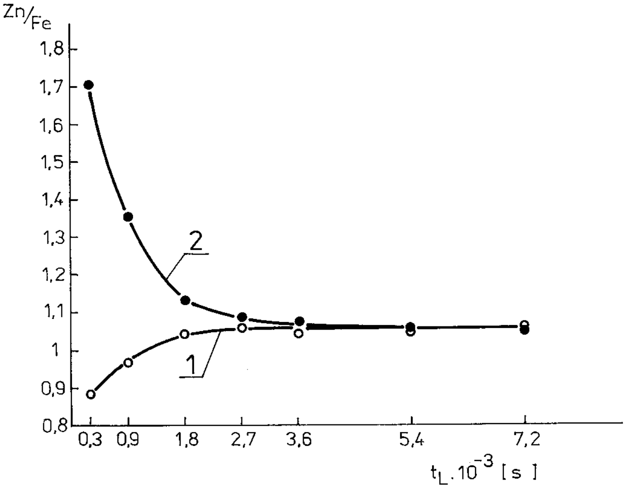

FIG. 8. Zn/Fe ratio in the solution vs dissolution time t_L determined at dissolution of the as-prepared sample of zinc ferrite in 0.5 *N*(1) and 1.5 *N*(2) sulfuric acid.

cific surface area and the inversion degree on the dissolution kinetics has been investigated. An exponential increase of the dissolution rate constant, k_{Zn+Fe}, with both parameters has been found,

$$\ln k_{Zn+Fe} = a + b\,X, \qquad [2]$$

where X is the specific surface area, S, or the inversion degree, δ determined for the investigated set of mechanically and thermally treated samples. For $X = S$, $a = 0.0147$ and $b = 0.1496$. When X represents the inversion degree, $a = 0.0138$ and $b = 2.1379$.

Selectivity of the dissolution characterized by $k_{Zn}/k_{Fe} = 1.3$ was found only at dissolution of the sample activated for 24 min (see Fig. 10). Its extreme reactivity, markedly different from that of other samples, was independently shown by the high-temperature XRD analysis (see again Figs. 7a and 7b).

The difference in granularity and inversion degree between 12 and 24 min ground samples are negligible and the inversion degree at heating to 600 K remains practically unchanged. In order to explain the extreme reactivity of the 24 min ground sample the mechanically and thermally induced changes in the structure of zinc ferrite should be taken into account.

According to data of Rietveld analysis reported in our previous works (10, 11) the mechanical activation results in a decrease in occupation factor of both zinc and iron cations in tetrahedral (A) and octahedral {B} positions. Except for the above changes indicating the mechanically induced inversion a decrease in unit cell dimension and oxygen parameter have been determined. In the process of mechanical activation the translation invariance of zinc ferrite structure is preserved. In addition to a small change in the length in tetrahedral bonds, the lattice contraction is accompanied mainly by deformation of octahedron: the shared octahedral edges become longer than the unshared ones. Since the distances tetra–tetra, octa–tetra, and octa/cation–octa/cation do not change, the change in octahedron geometry results in the alteration of the octa/cation–anion–octa/cation bond angle. It was also found that mechanically induced changes of zinc ferrite are caused by the onset of the intersublattice exchange interaction of the $Fe^{3+}(A)–O^{2-}–Fe^{3+}\{B\}$ type (with bond angle of 125°) taking place due to mechanically induced inversion as well as by the onset of intersublattice exchange interaction of the $Fe^{3+}\{B\}–O^{2-}–Fe^{3+}\{B\}$ type with deformed bond angles different from 90°.

Based on a model assuming the mechanically induced transition of all Zn^{2+} cations from tetrahedral into octahe-

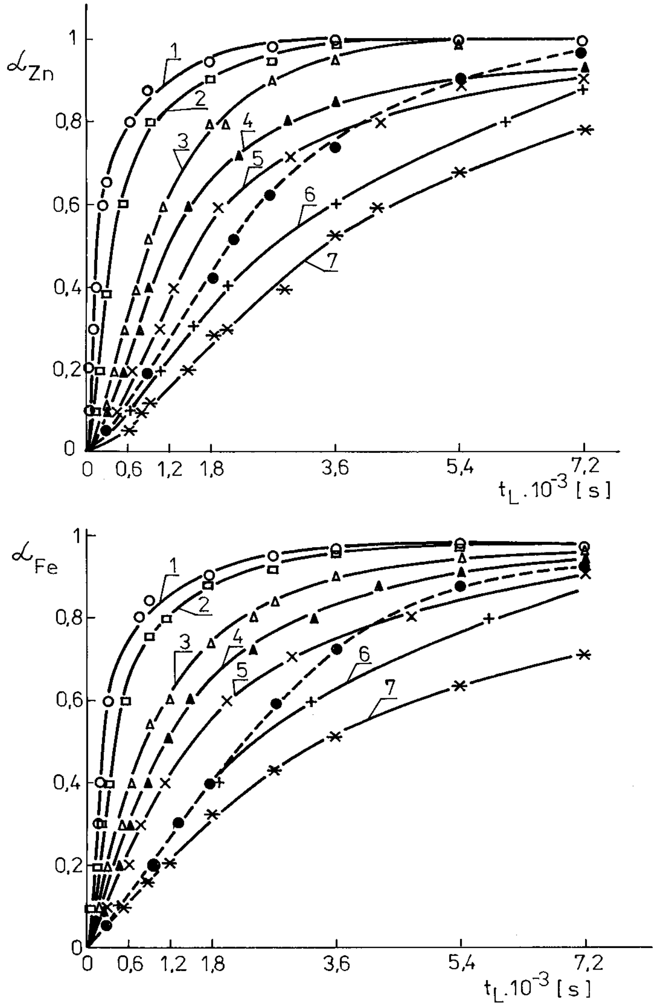

FIG. 9. Dissolution degree, α_{Fe} and α_{Zn}, vs dissolution time t_L for the sample mechanically activated for 24 min (1) and subsequently heated for 45 min at temperatures in K: 600 (2), 700 (3), 800 (4), 900 (5), 1000 (6), and 1200 (7). The dissolution kinetics of the as-prepared sample is indicated by full circles and dashed line.

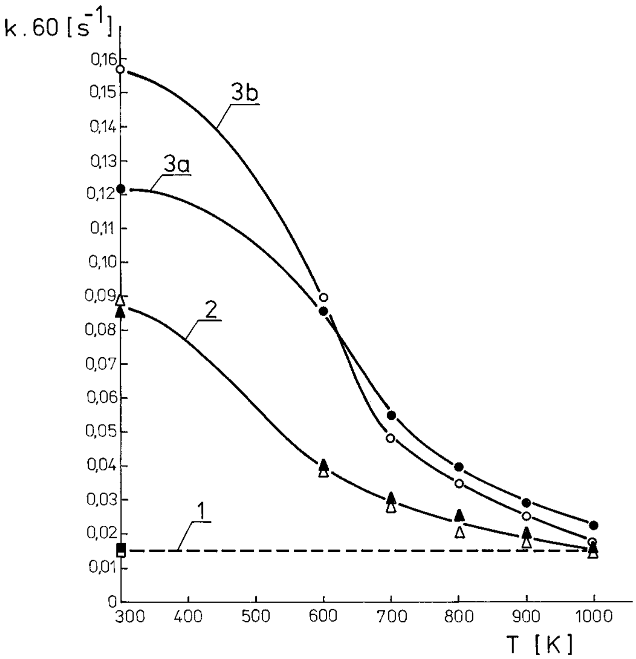

FIG. 10. Dissolution rate constant, k_{Zn} (empty points) and k_{Fe} (full points), vs temperature T for as-prepared sample (1) and samples mechanically activated for 12(2) and 24 min (3 a,b).

dral positions Pavlyukhin *et al.* (12, 24, 25) have calculated the number of octahedral sites corresponding to different cation–anion–cation bond angles (Table 1). According to these authors the Fe^{3+} {B}–O^{2-}–Fe^{3+} {B} interaction with bond angles 180° is responsible for the modified magnetic properties. Using the data from Table 1 the relative participation of these bonds was calculated according to

$$\begin{aligned} &p(\mathrm{c})\cdot k_{180}(\mathrm{c})/n(\mathrm{c}) + p(\mathrm{hex})\cdot k_{180}(\mathrm{hex})/n(\mathrm{hex}) \\ &\quad + p(\mathrm{h})\cdot k_{180}(\mathrm{h})/n(\mathrm{h}) \qquad [3] \\ &= 1/4\cdot 6/18 + 1/4\cdot 0/20 + 1/2\cdot 3/19 \approx 0.16. \end{aligned}$$

The deformation in octahedron geometry can be hypothetically connected with the selectivity of the cation dissolution and should be taken into account when trying to formulate preliminary conception on the reason of drastic decrease in the temperature of decomposition of zinc ferrite.

It may be assumed that the sites in a mechanically disturbed structure where the reaction of partial thermal decomposition is localized coincide with the sites showing maximum deformed bonds, i.e., cation–anion–cation bonds with an angle of 180°. These sites show maximum distortion of the structure and thermally induced alteration in the phonon spectrum of the lattice contributes to weakening of these bonds. It may be expected that these least stable bonds do not return into their initial positions (90°) upon heating and the relaxation of lattice strains occurs by the rupture of these bonds. Assumption that no other than 180° bonds are responsible for the partial decomposition of ferrite is supported also by the approximate correspondence between the relative participation of these bonds amounting to 16% (Eq. [3]) and the relative quantity of the decomposed ferrite which is about 14%.

The products of zinc ferrite decomposition were identified only at temperatures above 780 K. Consequently the decomposition takes place simultaneously with the return of zinc and iron cations from the inversion into equilibrium sites. Therefore, it can be assumed that the increased mobility of ions is also an important factor in the low-temperature thermal decomposition of mechanically activated zinc ferrite.

4. CONCLUSIONS

The transition of zinc ferrite into a metastable state is a result of a mechanically induced inversion and deformation in octahedron geometry. The mechanically induced inversion is reversible and the stresses around the deformed bonds may relax during heating. Chemical changes serve as one possible channel of the relaxation.

The rate of dissolution of zinc and iron in diluted acid

TABLE 1

Type of oxygen sublattice	Probability of the formation of a given type of oxygen sublattice p	Total number of nearest octa-sites for an arbitrarily chosen cation n	Number of octahedral sites, corresponding to cation–anion–cation bond angle			
			71° k_{71}	90° k_{90}	132° k_{132}	180° k_{180}
Cubic (*c*)	1/4	18	0	12	0	6
Hexagonal (*hex*)	1/4	20	2	6	12	0
Hybrid (*h*)	1/2	19	1	9	6	3

increases exponentially with increasing specific surface area as well as with increasing inversion degree of mechanically activated zinc ferrite. The deformation in octahedral geometry of zinc ferrite can be hypothetically connected with the selective promotion of the dissolution of Zn. The ratio of the dissolution rates, $k_{\mathrm{Zn}}/k_{\mathrm{Fe}} > 1$, can serve as an indicator of the formation of a metastable substance markedly differing from normal and partially activated zinc ferrite in structure and chemical behavior.

The extraordinary chemical behavior of mechanically activated zinc ferrite manifests itself in its decomposition at temperatures that are 50% lower than the temperature of its synthesis. Based on approximate correspondence between relative participation of the maximum deformed cation–anion–cation bonds with a bond angle 180° and a relative quantity of decomposed ferrite, these maximum deformed bonds can be assumed as the sites where the partial decomposition is localized. The decomposition takes place simultaneously with the return of Zn and Fe cations into equilibrium positions. The increased mobility of the cations in a narrow temperature range can be an important factor stimulating the low-temperature decomposition of mechanically activated zinc ferrite.

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